Ferromagnetism and Superconductivity in Carbon-Based Systems

Y. Kopelevich and P. Esquinazi*

Instituto de Física "Gleb Wataghin", Universidade Estadual de Campinas, Unicamp 13083-970, Campinas, São Paulo, Brasil
**Division of Superconductivity and Magnetism, Institut für Experimentelle Physik II, Universität Leipzig, Linnéstr. 5, D-04103 Leipzig, Germany*

In this article we shortly review previous and recently published experimental results that provide evidence for intrinsic, magnetic-impurity-free ferromagnetism and for high-temperature superconductivity in carbon-based materials. The available data suggest that the origin of those phenomena is related to structural disorder and the presence of light elements like hydrogen, oxygen and/or sulfur.
PACS numbers: 81.05.Uw, 75.50.-y, 74.70.-b

1. INTRODUCTION

In the last months of the year 1999 Frank Pobell, one of the editors of the Journal for Low Temperature Physics, received a manuscript entitled "Ferromagnetic- and Superconducting-Like Behavior of Graphite" to be considered for publication. In this manuscript[1] we reported on the possible occurrence of ferromagnetic as well as superconducting correlations in highly oriented pyrolytic graphite (HOPG) samples at ambient conditions. It is well known that graphite is the most diamagnetic material among non-superconducting substances and it lacks d- and f- electrons, which are generally assumed to be necessary for the occurrence of ferromagnetism at relatively high temperatures ($T > 15$ K). Materials that show superconducting properties at room temperature, on the other hand, were (and still are) rather unknown. At such circumstances, the skepticism expressed by

the referees of the above manuscript was understandable. The referees suggested that the observed ferromagnetic behavior of graphite was governed by magnetic impurities such as Fe, Fe_3O_4 or Fe_2O_3. In spite of the referee skepticism, the editors of the journal decided to publish our manuscript accompanied by the Editor's Note: "There has been a controversy between the opinions of the referees on the possible influence of impurities on the observations. However the editors have decided to publish this article because its content is of rather high significance and may stimulate further work and discussion". Certainly, we believe that the Editors decision was correct and therefore we take this opportunity to report on recent as well as rather unknown developments in this field, honoring Frank Pobell for his work as Editor of the Journal of Low Temperature Physics.

2. FERROMAGNETISM AND SUPERCONDUCTIVITY IN CARBON-BASED MATERIALS: HISTORICAL NOTE

2.1. Ferromagnetism

Ferromagnetism at high temperatures in carbon-based structures was reported in several tens of papers in the last millennium.[2] Unfortunately, a rigorous evaluation of those studies is not an easy task because in most of them there is no or a rather incomplete study of the impurity contents in the samples. Nevertheless, there are a few publications that speak for an intrinsic phenomenon. In 1987 Torrance et al.[3] reported that the reaction of symmetrical triaminobenzene ($C_6H_9N_3$) with iodine produces a black, insoluble polymer. This polymer showed, in some of the runs, ferromagnetism up to 700 K, which is near its decomposition temperature. Although some trace quantities of Fe were found, neither its amount nor the observed irreversibility in the magnetic moment as a function of temperature speak for magnetic impurities as the possible source for the magnetism. Apparently, a lack of reproducibility of the results reported by these authors remained in the years to come.

It appears that in several of the studies published in the last 20 years the problem of reproducibility of magnetic carbon was a general, major problem, which is not necessarily related to the inclusion or not of impurities but also to a rather narrow window of parameters necessary to produce the expected results. Even nowadays and in spite of the improvement in the characterization methods, we do not find yet a reliable method to produce magnetic order in carbon with high reproducibility.

In 1991 Murata et al.[4] measured the magnetization of amorphous-like carbons (amorphous carbon has localized π-electrons and its bonds are inconsistent with any other known allotrope forms of carbon) prepared from

tetraaza compounds (organic monomers with different amounts of carbon, hydrogen and nitrogen) by chemical vapor deposition method. The aza-carbon showed a magnetization of 0.45 emu/g at room temperature and at 50 Oe applied field. The saturation magnetization of the prepared films increased as a function of the ratio between hydrogen and carbon (H/C) of the starting material, up to values of the order of 10 emu/g (only a factor 10 smaller than the magnetization at saturation in magnetite).[5]

Murakami and Suematsu[6] produced magnetic ordering in fullerene crystals exposing them to light irradiation from a xenon lamp in the presence of oxygen. They showed that the typical diamagnetism was overwhelmed by a para- and ferromagnetic response after irradiation of the sample under xenon light in oxygen for 2.5 hs. The decrease of the magnetic moment (para- and ferro-magnetic contributions) after annealing and its increase after leaving the sample in air for three months speak against the contributions of Fe-impurities. A magnetic moment of 0.1 μ_B per C_{60} molecule was estimated from the separated magnetic part of the sample. The temperature dependence of the saturation magnetization indicates an extraordinarily high Curie temperature $T_c \sim 800$ K. Makarova et al.[7] reported recently similar effects for laser- and electron-beam-illuminated C_{60} films obtained either in air or oxygen-rich atmosphere.

2.2. Superconductivity

Superconductivity in carbon-based materials was first found in alkali-metal graphite intercalation compound (GIC) C_8K with a superconducting transition temperature $T_c = 0.15$ K.[8] Till very recently (see below), the highest $T_c = 5$ K was reached in the GIC C_2Na.[9] Afterwards, the research work on the superconductivity in carbon-based materials has been mainly focused on fullerene-based compounds, triggered by the observation of superconductivity in alkali-doped C_{60} (buckminsterfullerenes) at 18 K in K_3C_{60}[10] and at 33 K in $Cs_xRb_yC_{60}$.[11] An indication for high-temperature superconductivity in interhalogen-doped fullerenes has been reported by Song et al.[12] The interhalogen-doped fullerenes were prepared by using iodine monochloride (ICl) as a dopant. SQUID magnetization measurements revealed signatures of superconductivity with a superconducting transition temperature above 60 K. Apparently, the results were not reproduced afterwards and therefore this work remained rather unknown by the community. Antonowicz[13] on the other hand, reported on possible room-temperature superconductivity in aluminum-carbon-aluminum (Al-C-Al) sandwiches. As in Ref. 12, the study in Ref. 13 did not trigger a broad scientific interest. We note that superconductivity in many carbon-based materials is a metastable phenomenon and therefore a lengthy, systematic experimental work is needed.

3. FERROMAGNETIC ORDER IN CARBON STRUCTURES

3.1. Magnetic impurities

Iron is usually the main magnetic impurity one finds in carbon-based materials. Due to its relatively large para- and ferromagnetic contributions, the measurement of its concentration is of main importance. There are different methods to perform this measurement. In Ref. 14 Particle Induced X-ray Emission (PIXE) with protons was used to measure the magnetic impurities of different graphite samples. The results showed that for samples with concentration of Fe-impurities between 0.3 μg/g to 19 μg/g the magnetization at 2 kOe - after subtraction of background diamagnetic contribution - does not show any correlation with the Fe-concentration. The results also indicate that the ferromagnetic-like hysteresis loops are weakly temperature dependent between 5 K and 300 K. The assumption that such a small amount of Fe distributed in the carbon matrix behaves ferromagnetically is consistent neither with the observed temperature dependence nor with the behavior observed in graphite samples with much larger Fe concentrations.[14] To test the accuracy of the PIXE method used in Ref. 14, recent measurements have been performed on similar HOPG samples using neutron analysis and X-ray fluorescence. The three methods agree within experimental accuracy and indicate that, for example, HOPG samples of ZYA grade from Advanced Ceramics have a Fe concentration below 1 μg/g ($\sim$ 0.25 ppm). Because the magnetic moment due to the ferromagnetic part of carbon-based samples is usually small, great care must be taken with the measurement of the impurities in all steps of the sample handling.

3.2. Recent Reports

In the last five years there were several publications that indicate the existence of magnetic order at relatively high temperatures in carbon-based structures. One of the most cited papers on magnetic carbon was published after Ref. 1 and reports on magnetic studies of polymerized fullerene with a Curie temperature of 500 K.[15] Impurity measurements done on these samples after the publication revealed, however, that they had a considerable amount of Fe impurities,[16,17] clearly exceeding the one reported in the original publication.[15] Nevertheless, the measurement of magnetic-like domains in impurity free regions[18] left us with doubts whether the Fe impurities were responsible for the measured magnetic moment. Recent experiments performed on samples prepared with mixtures of Fe and fullerene under high temperatures and high pressures[19] indicate that the Fe particles transform totally in cementite Fe_3C with a Curie temperature of 500 K. These last results therefore leave no doubt on the origin of the magnetic signals in

the samples reported in Ref. 15. It should be noted, however, that the room-temperature ferromagnetism in pressure polymerized fullerenes was also reported in Refs. 20,21, in hydrofullerite $C_{60}H_{24}$ in Ref. 22 and photopolymerized fullerene powder and films in Ref. 7.

As mentioned in section 1.1., early literature on magnetism in carbon structures suggests that disorder and probably hydrogen or other light elements like oxygen play a role in the reported ferromagnetism. In particular, the work in Refs. 4,5 suggests a correlation between hydrogen concentration and magnetic order in carbon. Proton irradiation provides the unique possibility to implant hydrogen, to produce lattice defects in the carbon structure and to have simultaneously a complete elemental analysis of the magnetic impurities in the sample.

Protons in the MeV energy range have a penetration depth of several tens of micrometers inside a carbon structure. The defect formation process by high energy protons is a non-equilibrium athermal process and it appears rather unlikely that ordered arrays of defects are formed by migration of interstitial carbon atoms or vacancies, perhaps with the exception of interstitials across the gallery. In Ref. 23 a review of the published results is given. Although the number of variable irradiation parameters is large (energy, fluence, proton current, temperature and samples state and thermal coupling) it is shown that with implanted protons of the order of 100 μC or larger, observable effects are registered with the SQUID. More systematic studies including the use of different kinds of ions are necessary to understand the role of different irradiation parameters to trigger magnetic order in carbon structures.

Talapatra et al.[24] reported that Nitrogen and Carbon irradiation of nanosized diamond powder triggers magnetic order at room temperature. Whatever the origin for the observed phenomenon - in that study no impurity analysis was presented - the results indicate that further studies of irradiation effects on the magnetism of carbon-based as well as of other nominally non-magnetic materials will appear in the future.

The studies done in Ref. 25 reveal that carbon films prepared by CVD on stainless steel substrates reach magnetization values of the order of 0.15 emu/g at room temperature, comparable to those reported in earlier studies.[4,5] In that paper the amount of measured impurities appears to be not enough to account for the absolute value of the magnetic moments of the samples.

Aging as well as low-temperature annealing effects on the magnetic properties might be treated as experimental evidence against the metallic impurity magnetism in graphite and other carbon-based structures. These aging effects were reported for $C_{60}H_{24}$,[22] proton irradiated carbon structures[23]

and oxygen-driven ferromagnetism.[26] The oxygen effect on the magnetic properties of graphite has been explored in Ref. 26. In these experiments, an activated graphite powder was prepared by cutting and grinding an ultraclean graphite rod at $T = 300$ K in oxygen atmosphere by means of a virgin diamond saw blade. It is found that whereas the starting sample demonstrated a diamagnetic (non-hysteretic) response, measurements performed on the oxidized graphite powder revealed a pronounced ferromagnetic signal. It has been also found that the ferromagnetism vanishes with time after taking the sample out from the oxygen atmosphere, suggesting that the ferromagnetism is triggered by the adsorbed oxygen and not by a possible trace of magnetic impurities.

4. SUPERCONDUCTIVITY IN CARBON SYSTEMS: RECENT STUDIES AND OUTLOOK

Local superconductivity with T_c ranging from ~ 7 K to 65 K has been observed in sulfur-graphite composites (C-S).[27–31] The results indicate that the superconductivity occurs in a small sample fraction, possibly within filaments and/or at the sample surface. These observations suggest that adsorbed foreign atoms on the graphite surface can trigger both ferromagnetism and superconductivity. Besides, indirect evidence has been obtained that there is an interaction between the ferromagnetic and superconducting order parameters. In particular, it has been observed that the superconductivity occurrence in C-S rotates the ferromagnetic moment direction by 90° confining it within the graphite basal planes.[30]

The occurrence of superconductivity in carbon nanotubes (CNT), which are graphite sheets folded into a cylindrical shape, has been demonstrated by M. Kociak et al. at 0.55 K.[32] Other results suggest that superconducting correlations in CNT can take place at much higher temperatures, viz. at 20 K[33] and possibly even at room temperature.[34] An unambiguous evidence for the superconductivity with $T_c = 12$ K has been reported for multiwalled CNT.[35] In 2004, superconductivity with $T_c \sim 4$ K has been discovered in heavily boron-doped diamond synthesized at high pressure/high temperatures conditions.[36] Superconducting diamond films with higher T_c(~ 7 K, onset) were produced by a CVD method.[37]

Some progress has been achieved also in the synthesis of superconducting GIC. The superconducting intercalated compounds C_6Yb ($T_c = 6.5$ K) and C_6Ca with $T_c = 11.5$ K have been obtained in Refs. 38,39. Thus and in spite of previously obtained superconductivity in graphitic systems with higher T_c,[27–31] further experiments with GIC look promising.

In 1992 Agrait et al.[40] published scanning tunneling spectroscopy results

obtained on graphite surfaces at $T = 4.2$ K that revealed a gap (Δ) in the electronic structure of the order of 50 to 100 meV. The authors suggested that the gap originates from single electron charging effects, i.e. Coulomb blockade. In fact, multiple maxima, periodic in voltage, are seen in the DOS when contamination between the tip and the surface exists. However, a single maximum in the DOS was obtained. Interestingly, this kind of curves are not only reproducible but occurs only in disordered surface regions, which may indicate that either contamination produces an artifact or that the structure of disordered graphite has local properties similar to superconductors and/or strongly correlated systems.

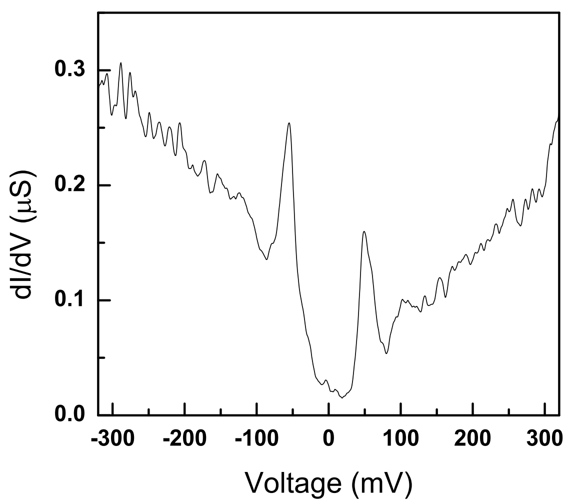

Fig. 1. "Anomalous" curve of differential conductance versus bias voltage obtained at 4.2 K with a Au tip on a graphite surface. This curve resembles that shown in Fig. 3(a) in Ref. 40. The curve is reproduced with permission of J. G. Rodrigo, Universidad Autónoma de Madrid.

Figure 1 shows recent results of DOS measurements performed by one of the authors of Ref. 40 on a pure graphite (HOPG) surface. Similar to the results of Ref. 40 the gap signature in dI/dV vs. V is very clear. It is tempting to conclude that well-defined peaks in the tunneling conductance are related to coherence peaks expected within the framework of the BCS theory for superconductivity. The value of the bias voltage that corresponds

to the peak of tunneling conductance is a good measure for the superconducting gap Δ_{sc}. Then, the superconducting transition temperature T_{sc} can be estimated from the BCS equation $2\Delta_{sc}/k_B T_{sc} \sim 3.5$. If the curve is due to a superconducting surface region of graphite, it would indicate an extremely large energy gap and consequently a very high critical temperature. Using the data of Fig. 1 and the above equation, one estimates $T_{sc} \sim 300 \ldots 400$ K. Alternative explanations for the gap are also possible. For instance, the gap shown in Fig. 1 may also be related to the Kondo effect observed in other carbon-based materials such as CNT[41,42] and C_{60}^{n}-molecule.[43] Magnetic field dependent measurements as well as measurements checking the state of the tip (by going back and forth to a known metallic surface region like Au) are necessary to understand the gap origin in graphite.

Finally, we would like to make a parallel between our studies[1] and earlier reports on the interplay between ferromagnetic- and superconducting-like behavior of oxidized atatic polypropylene (OAPP) and amorphous poly(dimethylsiloxane) (PDMS) polymers samples.[44–46] In both graphitic systems and the polymers, the occurrence of either ferromagnetic- or superconducting-like magnetization at room temperature depends on heat treatment, oxidation, light illumination, and time (aging effect). Besides, in the case of OAPP, a strong enough applied magnetic field could transform the superconducting-like $M(H)$ to the ferromagnetic-like $M(H)$ in an irreversible way, which has been attributed to the field-induced breaking of diamagnetic (superconducting) loops, resulting in a formation of ferromagnetic stripes.[44]

Atatic polypropylene (C_3H_6) is a linear hydrocarbon where the methyl groups are placed randomly on both sites of the chain. The atatic chains are soft and rubbery, and can be easily oxidized. Although not always measured, it is known that most of the studied graphitic samples contain a large amount of hydrogen.[47] So, the formation of similar C-H-O structures responsible for the magnetic (superconducting) behavior is possible in oxidized OAPP and graphite.

Our previous work[1] revealed that a low-vacuum heat treatment of HOPG samples can either enhance the ferromagnetic response or trigger superconducting-like $M(H)$ hysteresis loops at room temperature, once again suggesting that adsorbed light elements play a crucial role in the anomalous magnetic behavior of graphite. We may speculate that the aging effect, i.e. the time dependence of the sample magnetic response, is related to the oxygen adsorption-desorption and/or its migration to different defect sites. It is well known that graphite oxidation is triggered by the presence of surface defects. This makes us believe that a combined effect of structural disorder and adsorbed foreign atoms (molecules) such as S, H,

O (O_2) can be behind the anomalous magnetic behavior of graphite and related carbon materials. Then, it is not unreasonable to assume that aging effects, including the ferromagnetism $\rightarrow$ superconductivity transformation are related to migration of foreign elements on the sample surface. The very small ($\sim 0.01 \ldots 0.05\%$) Meissner fraction can also be understood assuming the formation of superconducting patches (filamentary loops[46]) at the graphite surface. The accumulated experimental evidence so far is certainly not enough to celebrate the discovery of the superconductivity at very high temperature. Further experimental work should concentrate on the production of the samples as well as characterization and reproducibility of the effects reviewed in this article.

5. CORRIGENDUM TO THE ORIGINAL PAPER OF Ref. 1

We take this opportunity to correct some erroneous data included in the original publication.[1] (a) In page 693 we have written that the Fe concentration of our HOPG-2 sample was 90 ± 26 ppm. This value has been obtained by means of spectrographic analysis. Measurements done on the same samples but with the PIXE analysis revealed that the Fe concentration was much smaller, namely 2 ± 0.5 ppm.[14] The reason for this huge discrepancy is unknown. Nevertheless, we stress that most of the HOPG samples we have measured show an extremely low Fe concentration, much lower than the values one finds in the literature. Because we have checked that our analysis method is reliable, we speculate that upon the used method, background contributions in the apparatus may give larger Fe concentration when the sample mass or size is too small.

(b) The superconducting-like hysteresis loops obtained after subtraction of the diamagnetic background and shown in Figs. 4, 5 and 7(a) in Ref. 1 are partially influenced by an artefact produced by the SQUID current supply.[48] This artefact is not due to the superconducting solenoid but it depends in a non-simple way on the maximum applied fields selected to measure the hysteresis.

ACKNOWLEDGMENTS

The authors gratefully acknowledge discussions with Dr. R. Höhne, Prof. S. Vieira, and Prof. S. Moehlecke. We thank Prof. J. G. Rodrigo from the Universidad Autónoma de Madrid for providing us with his unpublished STM data taken on graphite, especially that shown in Fig.1 of this manuscript and for stimulating discussions. This work was supported by the DFG under Le 758/20-1, CNPq and FAPESP.

REFERENCES

1. Y. Kopelevich, P. Esquinazi, J. H. S. Torres, and S. Moehlecke, J. Low Temp. Phys. 119, 691 (2000).
2. See for example the review by T. Makarova, Semiconductors 38, 615 (2004).
3. J. B. Torrance, S. Oostra and A. Nazzal, Synth. Metals 19, 709 (1987).
4. K. Murata, H. Ushijima, H. Ueda, K. Kawaguchi, J. Chem. Soc., Chem. Commun. 1265 (1991).
5. K. Murata and H. Ushijima and H. Ueda and K. Kawaguchi, J. Chem. Soc., Chem. Commun. 567 (1992).
6. Y. Murakami and H. Suematsu, Pure & Appl. Chem. 68, 1463 (1996).
7. T. Makarova, K.H. Han, P. Esquinazi, R. R. da Silva, Y. Kopelevich, I. B. Zakharova, and B. Sundqvist, Carbon 41, 1575 (2003).
8. N. B. Hannay, T. H. Geballe , B. T. Matthias , K. Andres , P. Schmidt , D. Macnair, Phys. Rev. Lett. 14, 225 (1965).
9. I. T. Belash, A. D. Bronnikov, O. V. Zharikov , A. V. Palnichenko, Solid State Commun. 64, 1445 (1987).
10. A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. Palstra, A.P. Ramirez, A. R. Kortan , Nature 350, 600 (1991).
11. K. Tanigaki, T. W. Ebbesen, S. Saito, J. Mizuki, J. S. Tsai, Y. Kubo, S. Kuroshima, Nature 352, 222 (1991).
12. L. W. Song, K. T. Fredette, D. Chung , and Y. H. Kao, Solid State Communications 87, 387 (1993).
13. K. Antonowicz, Nature 247, 358 (1974).
14. P. Esquinazi, A. Setzer, R. Hhne, C. Semmelhack, Y. Kopelevich, D. Spemann, T. Butz, B. Kohlstrunk, and M. Lsche, Phys. Rev. B 66, 46 (2002).
15. T. Makarova, B. Sundqvist, R. Hhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. A. Davydov, L. S. Kashevarova, and A. V. Rakhmanina, Nature 413, 716 (2001).
16. R. Höhne and P. Esquinazi, Adv. Mater. 14, 753 (2002).
17. D. Spemann, K.-H. Han, R. Höhne, T. Makarova, P. Esquinazi, and T. Butz, Nucl. Instrum. Meth. B 210, 531 (2003).
18. K.-H. Han, D. Spemann, R. Hhne, A. Setzer, T. Makarova, P. Esquinazi and T. Butz, Carbon 41, 785, see also 2425 (2003).
19. A. Talyzin, A. Dzwilewski, L. Drubovinsky, A. Setzer, and P. Esquinazi, http://arXiv.org/abs/condmat/0602306l.
20. R. A. Wood, M. H. Lewis, M. R. Lees, S. M. Bennington, M. G. Cain and N. Kitamura, J. Phys.: Condens. Matter 14, L385 (2002).
21. V. N. Narozhnyi, K.-H. Mller, D. Eckert, A. Teresiak, L. Dunsch, V. A. Davydov, S. Kashevarova and A. V. Rakhmanina, Physica B: Cond. Matt. 329, 1217 (2003).
22. V. E. Antonov, I. O. Bashkin, S. S. Khasanov, A. P. Moravsky, Yu. G. Morozov, Yu. M. Shulga, Yu. A. Ossipyan and E. G. Ponyatovsky, J. of Alloys and Compounds 330-332, 365 (2002).
23. P. Esquinazi, R. Hhne, K.-H. Han, D. Spemann, A. Setzer, M. Diaconu, H. Schmidt and T. Butz, in *Carbon based magnetism*, Elsevier Science, Eds. T. Makarova and F. Palacios, Chap. 19, 437 (2006).

24. S. Talapatra, P. G. Ganesan, T. Kim , R. Vajtai, M. Huang, M. Shima, G. Ramanath, D. Srivastava, S. C. Deevi, P. M. Ajayan, Phys. Rev. Lett. 95, 097201 (2005).
25. T. Saito, T. Ozeki, and K. Terashima, Solid State Commun. 136 , 546 (2005).
26. Y. Kopelevich, S. Moehlecke and R. R. da Silva, in *Carbon based magnetism*, Elsevier Science, Eds. T. Makarova and F. Palacios, Chap. 18, 417 (2006); cond-mat/0602415.
27. R. R. da Silva, H. Torres and Y. Kopelevich, Phys. Rev. Lett. 87, 147001 (2001).
28. Yang Hai-Peng, Wen Hai-Hu, Zhao Zhi-Wen and Li Shi-Liang, Chin. Phys. Lett. 18, 1648 (2001).
29. S. Moehlecke, Pei-Chun Ho, and M. B. Maple, Philos. Mag. B 82, 1335 (2002).
30. S. Moehlecke, Y. Kopelevich and M. B. Maple, Phys. Rev. B 69, 134519 (2004).
31. Y. Kopelevich, R. R. da Silva, J. H. S. Torres, S. Moehlecke and M. B. Maple, Physica C 408, 77 (2004).
32. M. Kociak, A. Yu. Kasumov, S. Guron, B. Reulet, I. I. Khodos, Yu. B. Gorbatov, V. T. Volkov, L. Vaccarini, and H. Bouchiat, Phys. Rev. Lett. 86, 2416 (2001).
33. Z. K. Tang, L. Y. Zhang, N. Wang, X. X. Zhang, G. H. Wen, G. D. Li, J. N. Wang, C. T. Chan, P. Sheng, Science 292, 2462 (2001).
34. G. M. Zhao and Y. S. Wang, cond-mat/0111268.
35. I. Takesue, J. Haruyama, N. Kobayashi, S. Chiashi, S. Maruyama, T. Sugai, and H. Shinohara, Phys. Rev. Lett. 96, 057001 (2006).
36. E. A. Ekimov, V. A. Sidorov , E. D. Bauer, N. N. Mel'nik, N. J. Curro, J. D. Thompson, S. M. Stishov, Nature 428, 542 (2004).
37. Y. Takano, M. Nagao, I. Sakaguchi, M. Tachiki, T. Hatano, K. Kobayashi, H. Umezawa, and H. Kawarada, Appl. Phys. Lett. 85, 2851 (2004).
38. T. E. Weller, M. Ellerby, S. S. Saxena, R. P. Smith, N. T. Skipper, Nature Physics 1, 39 (2005).
39. N. Emery, C. Herold, M. d'Astuto, V. Garcia, C. Bellin, J. F. Mareche, P. Lagrange, and G. Loupias, Phys. Rev. Lett. 95, 087003 (2005).
40. N. Agrait, J. G. Rodrigo and S. Vieira, Ultramicroscopy 42-44, 177 (1992).
41. J. Nygárd, D. H. Cobden and P. E. Lindelof, Nature 408, 342 (2000).
42. B. Babić, T. Kontos and C. Schönenberger, Phys. Rev. B 70, 235419 (2004).
43. Lorenzo De Leo and Michele Fabrizio , Phys. Rev. Lett. 94, 236401 (2005).
44. D. N. Rogachev and L. N. Grigorov, J. Superconductivity 13, 947 (2000).
45. L. N. Grigorov, Philos. Mag. B 78, 353 (1998).
46. D. M. Eagles, J. of Supercond. 15, 243 (2002); Philos. Mag. 85, 1931 (2005).
47. As an example of recent measurements see P. Reichart et al., Nuclear Instr. and Meth. B (2006, in press).
48. R. Höhne and P. Esquinazi, to be published.